

## 30 YEARS OF COSMIC FULLERENES

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**Abstract.** In 1985, “During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells”, Harry Kroto and his collaborators serendipitously discovered a new form of carbon: fullerenes. The most emblematic fullerene (i.e. C<sub>60</sub> “buckminsterfullerene”), contains exactly 60 carbon atoms organized in a cage-like structure similar to a soccer ball. Since their discovery impacted the field of nanotechnologies, Kroto and colleagues received the Nobel prize in 1996. The cage-like structure, common to all fullerene molecules, gives them unique properties, in particular an extraordinary stability. For this reason and since they were discovered in experiments aimed to reproduce conditions in space, fullerenes were sought after by astronomers for over two decades, and it is only recently that they have been firmly identified by spectroscopy, in evolved stars and in the interstellar medium. This identification offers the opportunity to study the molecular physics of fullerenes in the unique physical conditions provided by space, and to make the link with other large carbonaceous molecules thought to be present in space : polycyclic aromatic hydrocarbons.

Keywords: subject, verb, noun, apostrophe

### 1 The presence of large carbonaceous molecules in space : the PAH hypothesis

About 30 years ago, the presence of bands in emission (the strongest of which are found at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7  $\mu\text{m}$ ) in the mid-infrared spectrum of our Galaxy was observed. Soon after that, it was proposed by L ger & Puget (1984) and then Allamandola et al. (1985) that these bands result from the emission of large carbonaceous molecules from the family of Polycyclic Aromatic Hydrocarbons (PAHs), present in the gas phase and heated by the absorption of single UV photons. Since then, PAHs have been invoked to be part of numerous key processes in interstellar and circumstellar environments (e.g. the formation of H<sub>2</sub>, heating of the neutral gas, UV extinction etc.) and are widely used as tracers of physical conditions and star-formation in galaxies. Yet, even though it is widely accepted, the gas phase PAH model remains an hypothesis because no specific PAH molecule could be identified up to date. This is mainly because there exists a large number of PAH molecules (it is a “family” of molecules) and the broad mid-infrared emission bands are not specific enough to identify individual species from the PAH family.

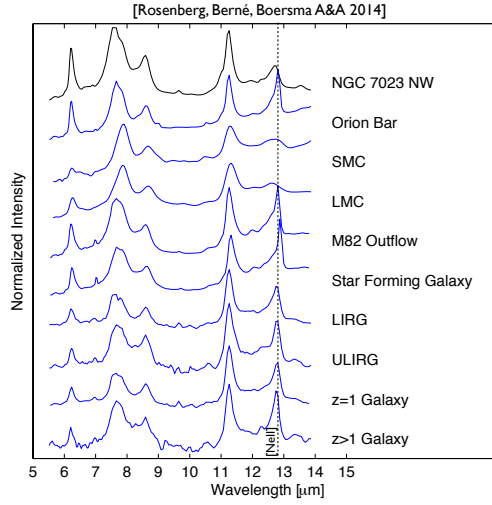
### 2 The serendipitous discovery of the C<sub>60</sub> molecule

About at the same time the PAH model was proposed, H. Kroto and his collaborators serendipitously formed, in the laboratory, a new molecule made of 60 carbon atoms arranged as the vertices of a soccer ball (C<sub>60</sub>, Fig. 2). It is worth noting that, in the original Nature paper (Kroto et al. 1985), the authors of the discovery present a photograph of a soccer ball as their Fig. 1. Because of the resemblance of the geometry of this molecule with the buildings of architect Buckminster Fuller, they coined the name “Buckminsterfullerene” for this new molecule. In fact, there exists a whole class of pure carbon molecules with icosahedral geometries of different

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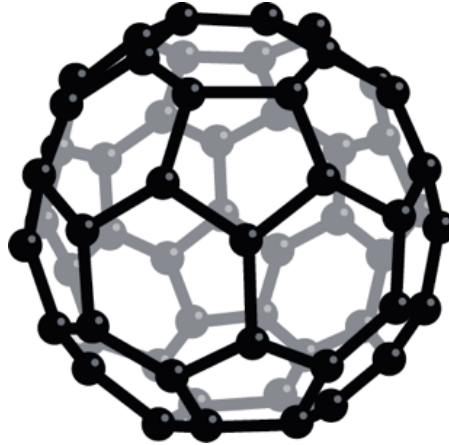
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**Fig. 1.** Mid-infrared spectra of UV-irradiated regions in the Milky Way and other galaxies obtained with the IRS instrument on-board the Spitzer Space Telescope and showing the main PAH bands. (see Rosenberg et al. 2014 for details).

sizes and shapes, which belong to the family of fullerenes. The discovery of  $C_{60}$  and fullerenes had a strong impact on the development of nanotechnologies, and H. Kroto and his colleagues received the Nobel prize in 1996 for this discovery. Yet, it should not be forgotten that, in their 1985 paper, the future Nobel laureates start their article by “During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells”, i.e. that their main goal was to understand interstellar and circumstellar chemistry.



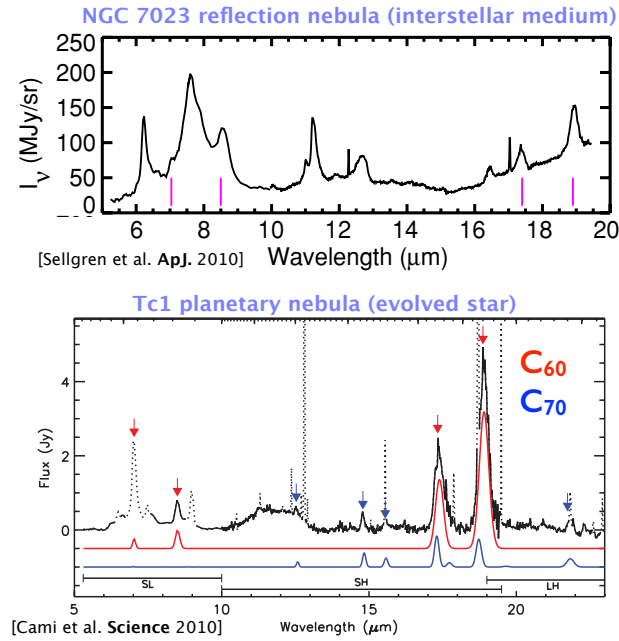
**Fig. 2.** Structure of the  $C_{60}$  molecule, “Buckminsterfullerene”. Figure credit L. Cadars.

### 3 The search and discovery of $C_{60}$ in space

$C_{60}$  has been sought for by astronomers since its discovery in 1985. The first serious evidence of the presence of  $C_{60}$ , in reality its cation i.e.  $C_{60}^+$ , was given by Foing & Ehrenfreund (1994) who detected two weak absorption bands in the diffuse interstellar medium with wavelengths close to those measured in the laboratory for the electronic transitions of  $C_{60}^+$ . Unfortunately, the laboratory data was obtained using matrix isolation techniques, which do not allow a precise enough measurement of the band positions for a definitive identification. Therefore,

this detection remained debated for nearly two decades. It was only in 2010 that clear evidence for the presence of  $C_{60}$  was provided. This time, it was with the detection in emission of the main vibrational bands (Fig. 3) of the neutral  $C_{60}$  molecule, in two reflection nebulae by Sellgren et al. (2010) and in an evolved star by Cami et al. (2010). While this discovery was an important step, it raised a number of question for astrochemistry :

- How is  $C_{60}$  formed in space ?
- $C_{60}$  was detected in its neutral form, while given the harsh conditions of the ISM one could expect to detect the cationic form of the molecule, i.e.  $C_{60}^+$
- It was proposed by Sellgren et al. (2010) that  $C_{60}$  is in the gas phase and heated by single UV photons, as in the PAH model, but Cami et al. (2010) suggested that  $C_{60}$  is stuck on the surface of grains at thermal equilibrium with the radiation field.

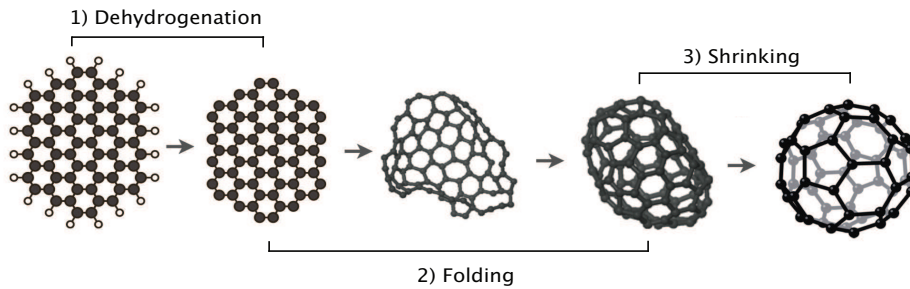


**Fig. 3.** Spitzer spectra of the NGC 7023 reflection nebula and TC 1 planetary nebula in which the main signatures of the  $C_{60}$  molecule are observed. In the case of NGC 7023, the PAH bands are also present. Figures from Sellgren et al. (2010) and Cami et al. (2010).

#### 4 The formation of $C_{60}$

One question related to fullerenes, and in particular  $C_{60}$ , concerns their formation pathway. Recently, “top-down” schemes where larger carbon clusters shrink to reach  $C_{60}$  have been proposed (Chuvilin et al. 2010; Zhang et al. 2013; Pietrucci & Andreoni 2014), and can be opposed to the traditional “bottom-up” approach where  $C_{60}$  is built up from small gas-phase species (Kroto & McKay 1988; Heath 1992; Hunter et al. 1994; Dunk et al. 2013). Using infrared observations of the NGC 7023 nebula, Berné & Tielens (2012) found evidence of an increase of the abundance of  $C_{60}$  with increasing UV field, while the abundance of PAHs decreases. This was interpreted by these authors as evidence for the formation of  $C_{60}$  from large PAHs ( $N_C > 60$ ) under UV irradiation, a top-down mechanism similar to the one observed by Chuvilin et al. (2010). García-Hernández et al. (2010, 2011) and Micelotta et al. (2012) proposed a similar mechanism where the starting materials are more complex, such as hydrogenated amorphous carbon instead of PAHs. Top-down scenarios are particularly appealing, given that the densities prevailing in the ISM are many orders of magnitude too low to allow for a bottom-up formation (i.e. starting from small gas-phase species) over reasonable timescales. Berné et al. (2015) proposed the first detailed model of the top-down photochemistry of interstellar fullerenes (Fig. 4). PAHs are

assumed to be formed in the envelopes of evolved stars (Frenklach & Feigelson 1989; Cherchneff et al. 1992; Merino et al. 2014) and then to be injected in the ISM. According to Berné et al. (2015), under UV irradiation, large PAHs, ( $60 < N_C \lesssim 1000$ ) are first fully dehydrogenated into small graphene flakes, dehydrogenation being by far the dominant dissociation channel (see Montillaud et al. 2013, and references therein). Additional UV irradiation enables these flakes to fold into closed cages. Once the cages are closed, they can lose  $C_2$  units if they continue to absorb energy (Irle et al. 2006). Because of the low densities prevailing in the ISM, the reverse reaction, that is, addition of  $C_2$ , is too slow to balance photodissociation and therefore the molecule will shrink. Once a system has reached  $C_{60}$ , it will remain in this form for a very long time because it is remarkably stable. Berné et al. (2015) find that, with this route, it is possible to convert about 1% of the interstellar PAHs into  $C_{60}$ . This efficiency results in predicted abundances that are comparable to the observed ones. It should be noted that  $C_{60}$  was recently formed in the laboratory (Zhen et al. 2014) in a top down manner similar to the one described in this theoretical model, i.e. from the irradiation of PAH molecules in the gas phase. However, the detailed steps taken to convert PAHs to  $C_{60}$  in this top down scheme are still a subject of debate within specialists (see discussion in Berné et al. 2015).



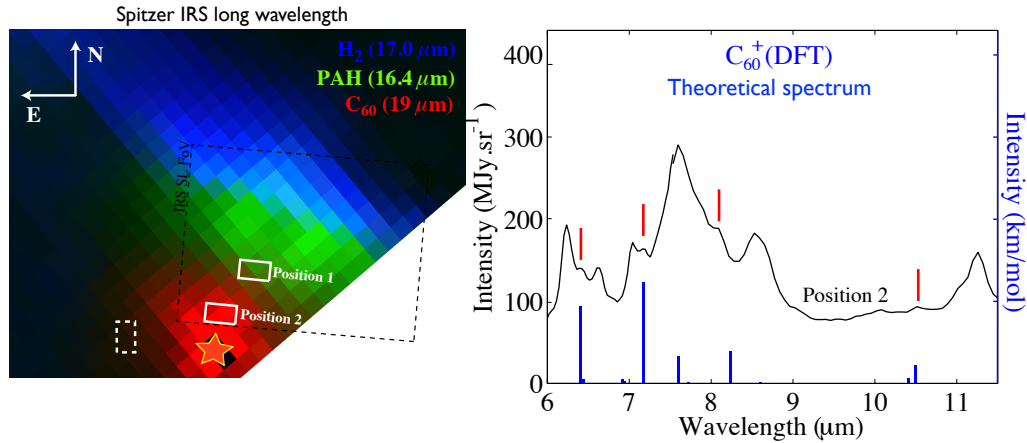
**Fig. 4.** Schematic representation of the evolutionary scenario for the “top-down” formation of fullerenes from PAHs under UV irradiation. From Berné et al. (2015).

## 5 The detection of $C_{60}^+$

Recently, Berné et al. (2013) examined in detail the *Spitzer* IRS spectra of the NGC 7023 reflection nebula, at a position close ( $7.5''$ ) to its illuminating B star HD 200775, and found four previously unreported bands at 6.4, 7.1, 8.2, and  $10.5 \mu m$  (Fig. 5), in addition to the classical bands attributed to PAHs and neutral  $C_{60}$ . These 4 bands are observed only in this region of the nebula (Fig. 5), while  $C_{60}$  emission is still present slightly farther away from the star, and PAH emission even farther away. Based on this observation Berné et al. (2013) suggested that these bands could be due to  $C_{60}^+$ . In addition, they conducted quantum chemistry calculations to determine the theoretical positions of the  $C_{60}^+$  bands. These theoretical band positions were found to match very well with the observed ones (Fig. 5). On this basis, Berné et al. (2013) concluded that the cationic form of  $C_{60}$ , i.e.  $C_{60}^+$  is also present in the ISM. In 2015, further evidence for the presence of  $C_{60}^+$  in the ISM was provided by Campbell et al. (2015) who measured in the laboratory a gas phase electronic spectrum of  $C_{60}^+$ . The measured positions of the electronic bands were found to be in very good agreement with the bands observed by Foing & Ehrenfreund (1994) (See sect. 3). The detection of an ion,  $C_{60}^+$ , in emission, confirms the idea that large carbon molecules exist in the gas phase in the ISM and that their emission is caused by the absorption of individual UV photons as initially suggested by Sellgren et al. (2010). This brings strong evidence that the PAH model (Sect. 1) is correct.

## 6 Conclusions

30 years after it was discovered in the laboratory, there is now convincing evidence that  $C_{60}$  and likely other fullerenes are present in space (indeed there is evidence for  $C_{70}$  in TC1, see Fig. 3). In the ISM,  $C_{60}$  is probably formed by a top down mechanism from PAHs, but it is possible that other mechanisms are at play in the dense envelopes of evolved stars. It was shown that  $C_{60}$  exists in the gas phase in the ISM and is heated by single UV photons emitted by massive stars. This confirms the emission mechanism put forward by the PAH model 30



**Fig. 5.** *Left:* False-color image of the NGC 7023 nebula such as the one presented in Sellgren et al. (2010), obtained from integrating different components in the *Spitzer*-IRS LL spectral cube. Red is the emission integrated in the  $\text{C}_{60}$  19  $\mu\text{m}$  band. Green is the emission of the PAH 16.4  $\mu\text{m}$  band. Blue is the emission integrated in the  $\text{H}_2$  (0-0) S(0) 17.0  $\mu\text{m}$  band. *Right:* Spectrum at positions 1 (see Berné et al. 2013 for spectrum at position 2) in the image. Error bars are not shown here but are comparable to the width of the line. The red lines indicate the four newly detected bands attributed to  $\text{C}_{60}^+$ . The DFT calculated spectrum is shown as a bar graph in blue. See Berné et al. (2013) for details.

years ago. The presence of neutral and cationic fullerenes indicates that the molecule is stable in both states and that the ionization fraction of  $\text{C}_{60}$  will depend on the local physical conditions. This opens the possibility to use  $\text{C}_{60}$  and  $\text{C}_{60}^+$  emission bands as a proxy of the physical conditions, mainly radiation field which controls the ionization and gas density which controls the electron recombination rate.

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